Materials 218/Chemistry 277UCSB: High T_C copper oxide superconductors and CMR:

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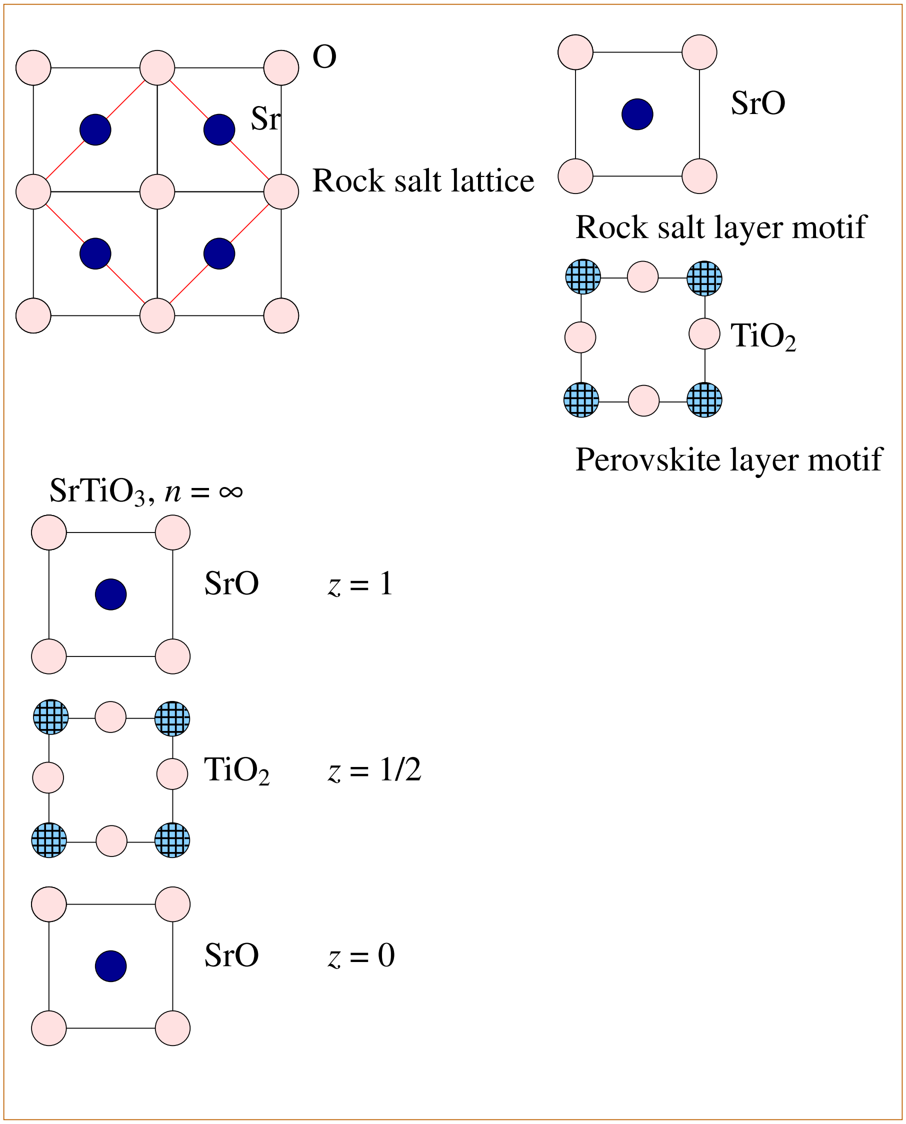
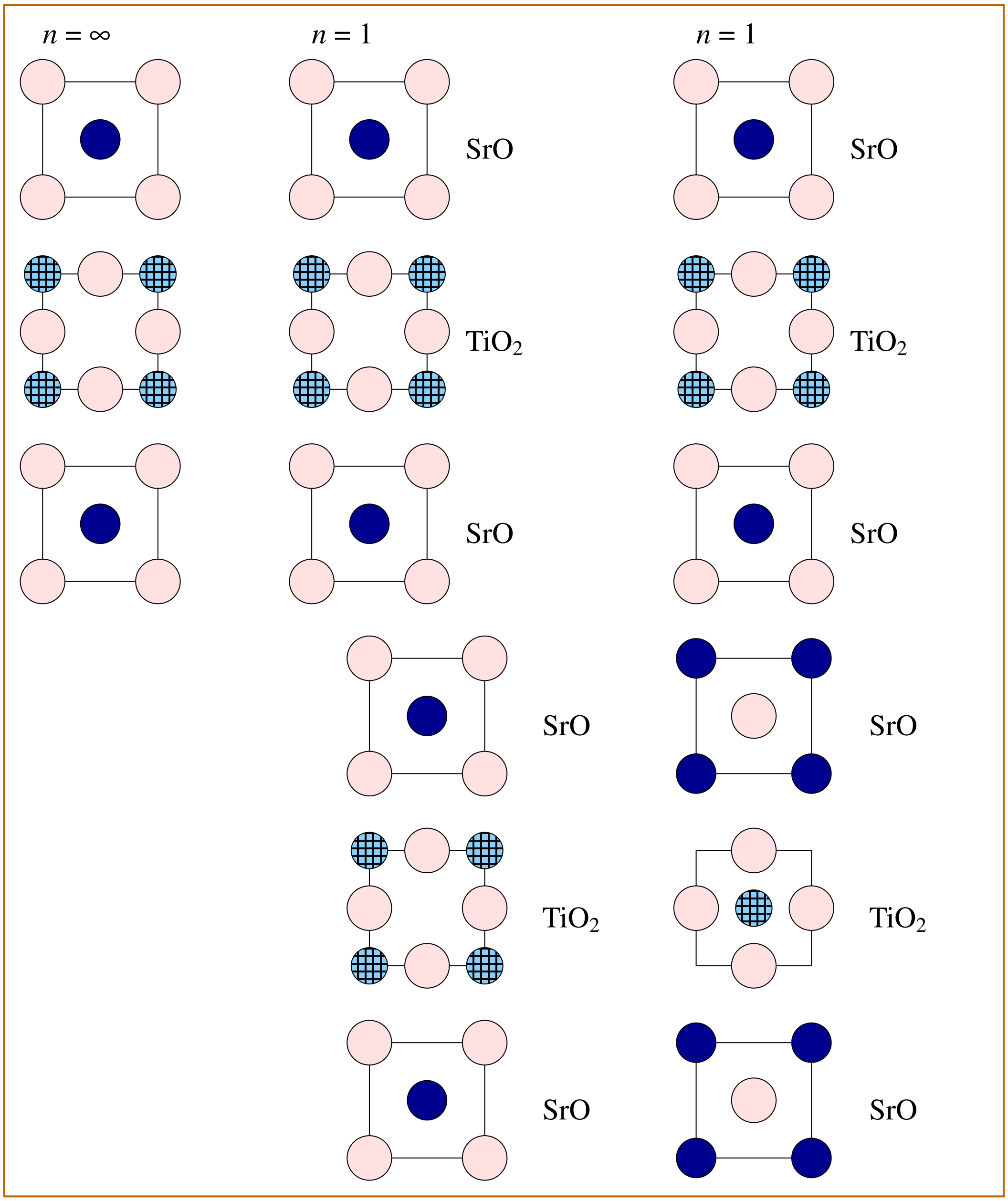
- The Ruddlesden-Popper phases:

  Ruddlesden-Popper phases are intergrowths of perovskite slabs with rock salt slabs. First described in the system Sr-Ti-O, the general formula of the the n^{th} member of the phase is $(\text{SrTiO}_3)_n(\text{SrO})$, and is also written, $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$. The perovskite structure is one end-member of the R-P series ($n = \infty$) and the K_2NiF_4 structure is the other end-member ($n = 1$). The $n = 0$ member is rock-salt.

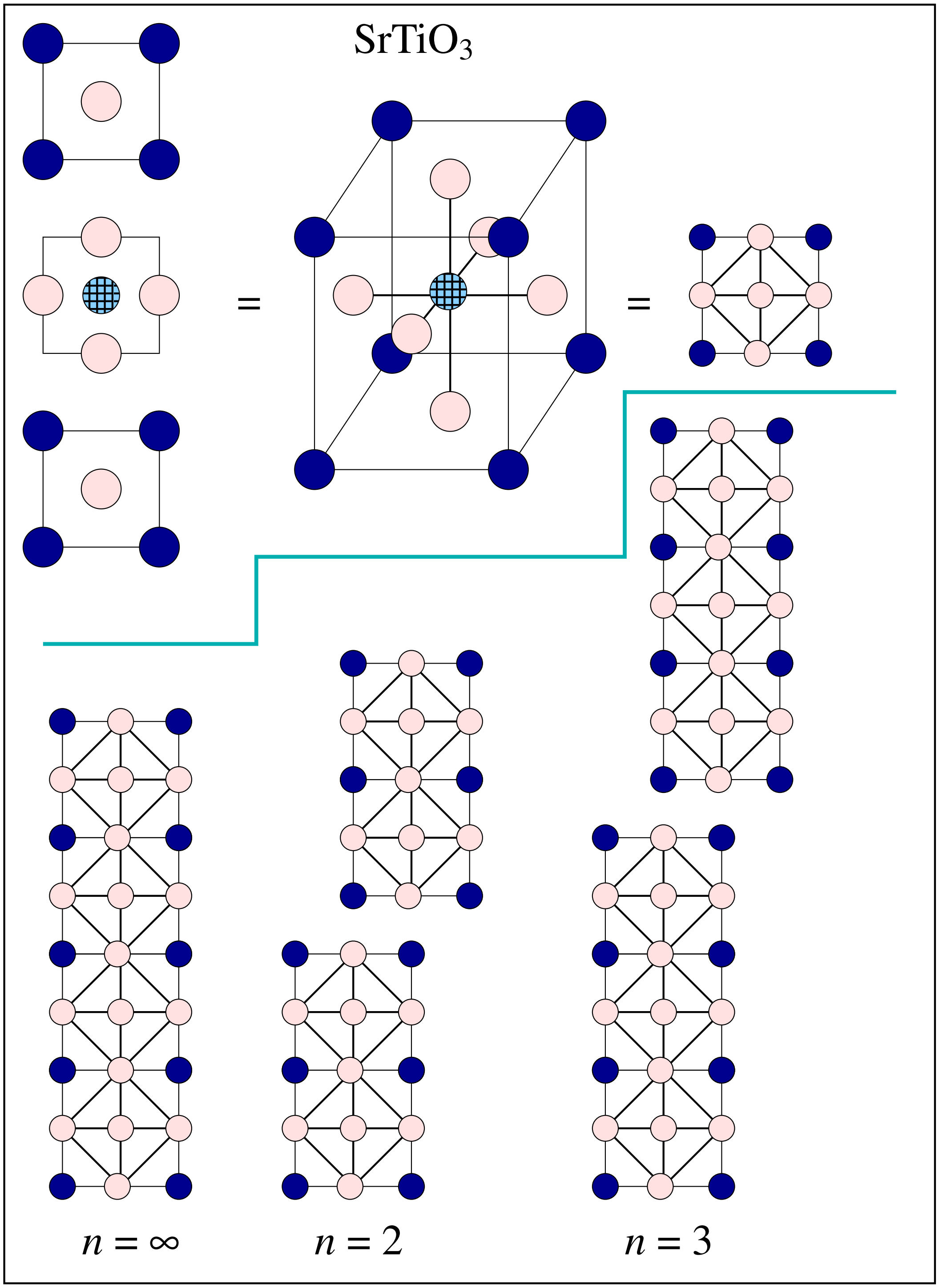
  We now consider different stacking depictions of the perovskite (SrTiO_3, $n = \infty$) phase and K_2NiF_4 (Sr_2TiO_4, $n = 1$) phases.





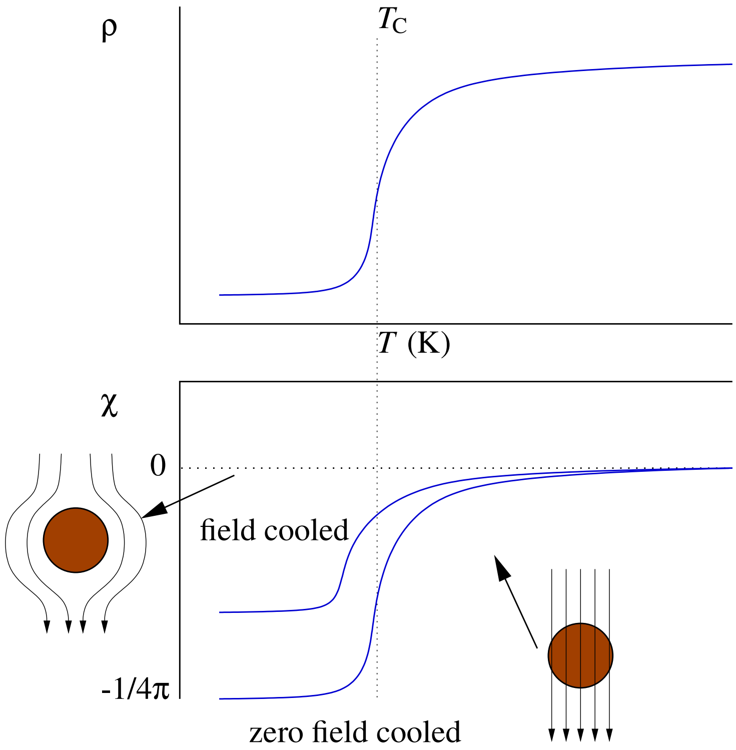
- Along the c axis (the stacking direction), we notice for $SrTiO_3$ ($n = \infty$), the repeat sequence is $\ldots$[SrO][TiO_2][Sr0][TiO_2]$\ldots$
- Along the c axis (the stacking direction), for Sr_2TiO_4 ($n = 1$), the repeat sequence is $\ldots$[SrO][SrO][TiO_2][Sr0][SrO][TiO_2]$\ldots$
- For $Sr_3Ti_2O_7$ ($n = 2$), the repeat sequence must be $\ldots$[SrO][SrO][TiO_2][SrO][TiO_2][SrO][SrO][TiO_2][SrO][TiO_2][SrO][SrO]$\ldots$

  There is an alternate way of visualizing these structures, making use of octahedra:



Superconductivity

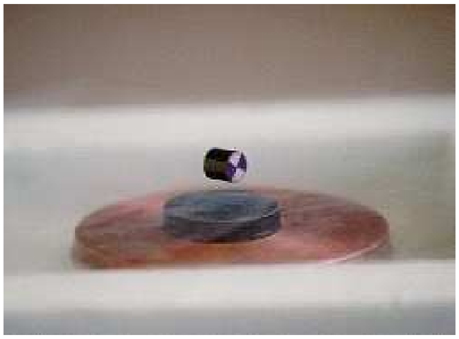
- In 1908, Kamerlingh Onnes liquefied He for the first time, and in 1911 he used it to cool mercury to about 1.5 K. At 4.2 K, the resistance of his Hg specimen dropped suddenly from about 0.1 Ω to 10^{-5} Ω, and by 3 K had dropped to $1/10^6$ its value at room T. This marked the discovery of superconductivity. Typical temperature dependence of the electrical resistivity and the magnetic susceptibility of a superconductor are shown below:



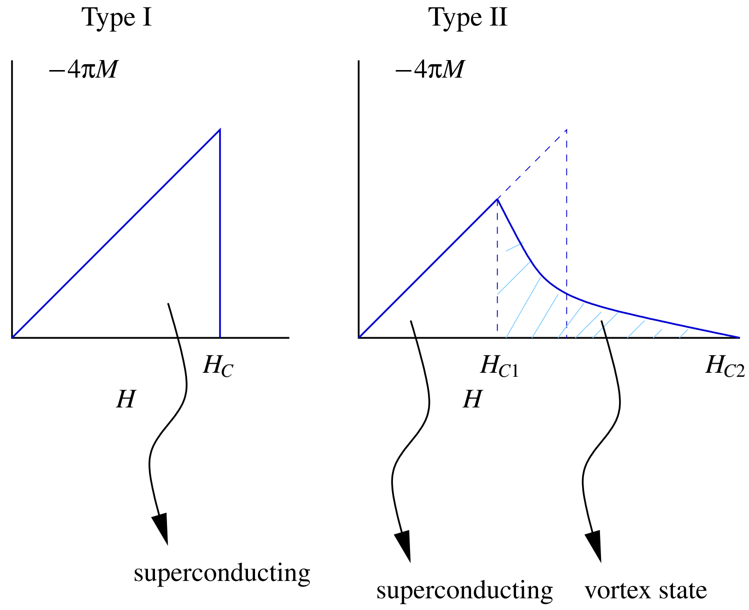
- Not only does the electrical resistivity go to zero, but because of the *Meissner effect* any magnetic lines of force are thrown out by the superconductor, making superconductors strong diamagnets (perfect, even, when the magnetic susceptibility becomes $\chi = -\frac{1}{4\pi}$).

- Uses of superconductors:

  - Used in electromagnetic coils in high field magnets in NMR, MRI *etc*.
  - Power transmission (high currents through thin wires)
  - Magnetic levitation

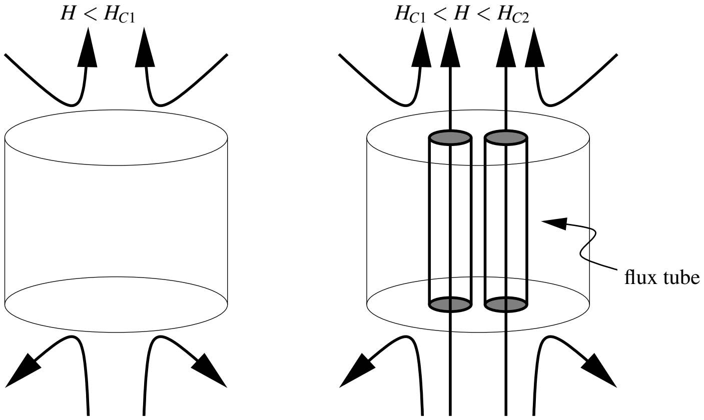


- Type I and type II superconductors:



In type I superconductors (pure metals), the superconductivity is destroyed by small magnetic fields; above some critical magnetic field H_C, the material is no longer superconducting. Typical critical fields are of a 1000 Oe.

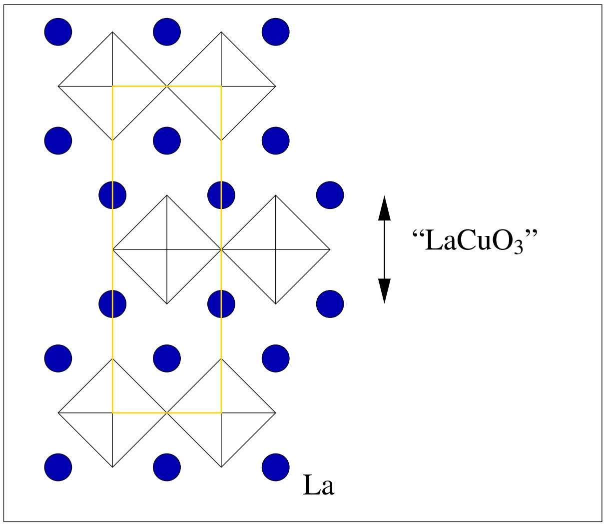
In type II superconductors, above the first critical field H_{C1}, the material is no longer a pure superconductor. It is in what is called the vortex state, comprising regions that are superconducting, interspersed with "flux tubes" that are normal (not superconducting). The magnetic field can penetrate the superconducting sample through the flux tubes, which often form an ordered lattice.

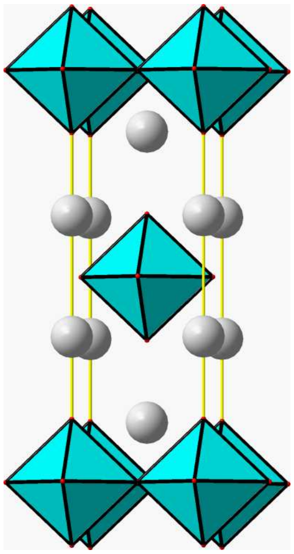


Examples of type II superconductor are most superconducting alloys and intermetallics (such as the so-called A15 compounds) and the high T_C copper oxide superconductors. The record for the second highest critical field H_{C2} is held by the Chevrel phase $PbMo_6S_8$ of 54 T at 4 K. Such materials are good candidates for forming superconducting solenoids.

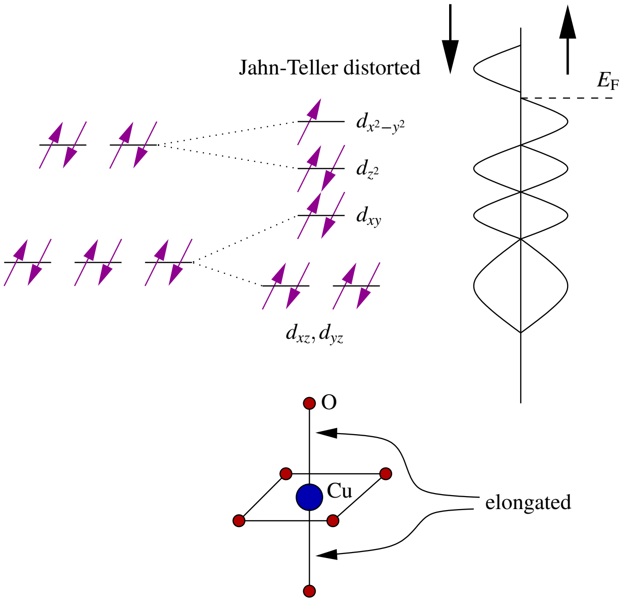
- $La_{2-x}A_xCuO_4$ (A = Sr, Ba *etc.*):

  The compound La_2CuO_4 has the K_2NiF_4 structure, which is the structure of the $n = 1$ Ruddlesden-Popper phase $(SrTiO_3)_1(SrO)$. A sketch as well as the "real" structure are shown below:





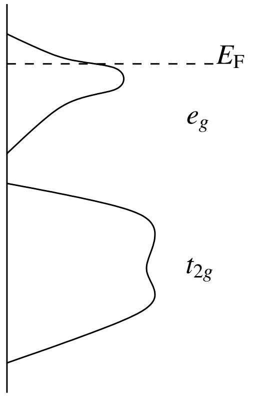
The large spheres are the La^{3+} ions. The formula suggests that in La_2CuO_4, Cu is in the +2 oxidation state. Cu^{2+} has 9 d electrons. Since it is octahedral, we would expect the crystal field diagram and the DOS to look as follows:



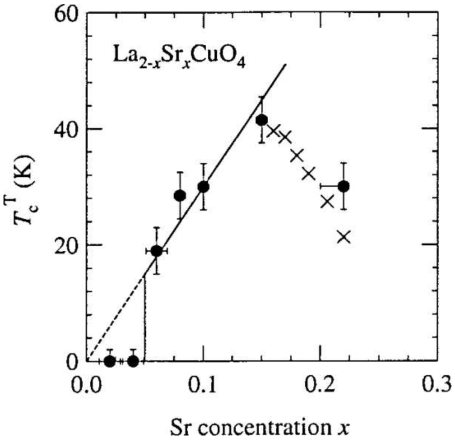
- The d^9 configuration is Jahn-Teller active. A Jahn-Teller active atom or ion has degenerate electronic states, and whose degeneracy can be lifted through a suitable structural distortion. In the case of a compound like La_2CuO_4, the degeneracy of the d^9 Cu is lifted by distorting the CuO_6 octahedra through elongation of the apical bonds. Jahn-Teller distortions of this kind (called 4-in, 2-out) split the t_{2g} and e_g levels by stabilizing those orbitals that have a z component. Thus, among the t_{2g} levels, d_{xz} and d_{yz} are stabilized, and d_{xy} is destabilized. Among e_g levels, d_{z^2} is stabilized and $d_{x^2-y^2}$ is destabilized.

  To construct the electronic structure of La_2CuO_4, we must first recognize that it is J-T active, and then we must switch on spin-polarization (because d^9 is magnetic for the first row transition metals). The combination of the JT distortion and the spin-polarization gives an insulator. Experiments confirm that La_2CuO_4 is in addition, antiferromagnetic.

- Changing (increasing) the oxidation state of Cu, by substituting some of the La^{3+} by suitable divalent ions A^{2+} (A = Ca, Sr, Ba) results in the system becoming a non-magnetic metal.[1] In addition, it displays superconductivity. This was the discovery of Bednorz and Müller in 1996 in the system $La_{2-x}Ba_xCuO_4$.
- Schematic DOS of $La_{2-x}Sr_xCuO_4$ is shown below:



- The phase diagram for the system $La_{2-x}Sr_xCuO_4$ is shown below:



- Note various special aspects of the perovskite derived structure that are essential for superconductivity to manifest in this system. Firstly, substitution at the A site (Sr-for-La) can be used to change the oxidation state at the B site (Cu). If the substitution were made at the B site, the electronic structure is "interrupted" and superconductivity cannot easily exist. The second feature is the presence of the CuO_2 square lattice that permits very disperse bands to be formed between Cu $d_{x^2-y^2}$ orbitals and O p_x and p_y orbitals (remember Assignment 5). This is considered to be an important ingredient of superconductivity.
- For high T_C superconductivity in the layered copper oxides, some other important criteria include:
  - That Cu forms quite covalent bonds with O, particularly when its oxidation state is high (between 2 and 3).
  - That Cu, being near d^9 is not very magnetic. Fe, Co and Ni compounds in the same structure and oxidation state are magnetic. Magnetism and superconductivity are usually competing states.
- Many other layered copper oxides (than the system $La_{2-x}A_xCuO_4$) are now known that display superconductivity with high transition temperatures.

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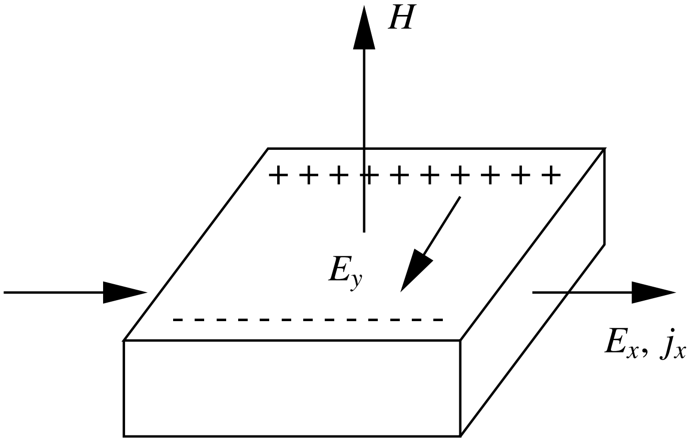
[1] Why does it become non-magnetic ? Firstly, a system with only 1 unpaired electron is not a very strong magnet,o it does not need a great deal to switch off the magnetism. Secondly, the process of making some of the electrons mobile through the Sr-for-La substitution results in (a) the magnetism being further weakened and (b) the bands become broader, switching off the magnetism completely.

- The most studied example, is the triple perovskite (with oxygen defects) $\mathrm{YBa_2Cu_3O_{7-\delta}}$ ($\delta \sim 0.05$) that has a critical temperature of 92 K.

Colossal magnetoresistance (CMR):

- The simplest example of magnetoresistance is *transverse* magnetoresistance associated with the Hall effect:



When an electrical conductor is subject to an electric field E_x along x and simultaneously, a magnetic field H along z, a new transverse field arises due to the Lorentz force of H on the electrons moving along x. This field E_y acts along y (because the Lorentz force is a cross product) giving rise to the Hall voltage. There is a magnetoresistance associated with the transverse field.

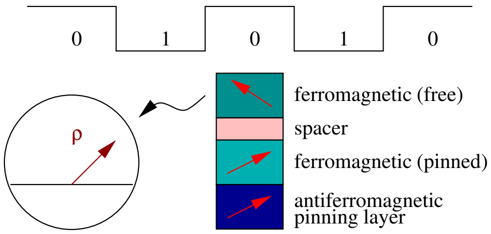
Such magnetoresistance measurements allow the number of free carriers to be obtained experimentally, as well as allow mapping of the Fermi surface *etc.*

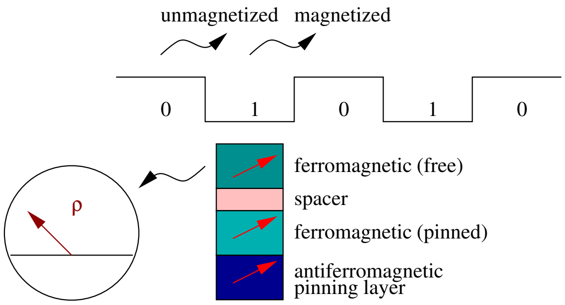
- Negative magnetoresistance is the term given to the large *decrease* in the electrical resistance when certain systems are exposed to a magnetic field. The (negative) magnetoresistance is usually defined as a percentage ratio:

$$MR = -\frac{\rho(0) - \rho(H)}{\rho(0)} \times 100\%$$

where $\rho(H)$ is the resistivity in the presence of a magnetic field of strength H and $\rho(0)$ is the resistivity in the absence of a magnetic field.

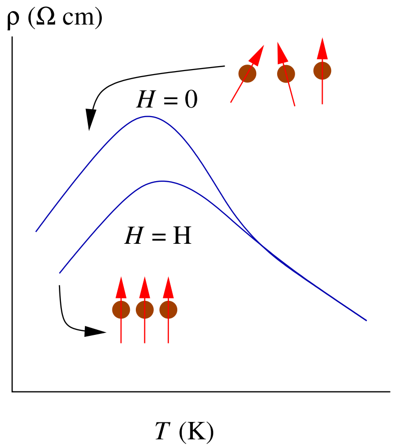
- The term Giant Magnetoresistance (GMR) has come to be associated with certain thin metallic multilayer devices that are commonly used in the read-heads of magnetic hard disks.



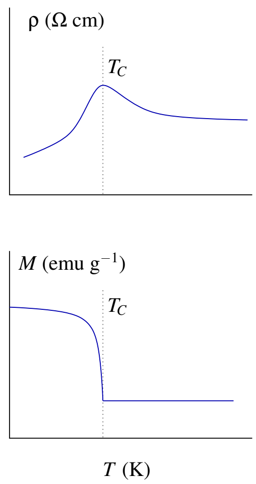


When the head (the free ferromagnetic layer) runs over a magnetized region on the hard disk, the magnetization of the magnetic layer is aligned with the magnetization of the pinned magnetic layer. This reduces the electrical resistivity of the assembly.

- Many ferromagnetic elements display an intrinsic negative magnetoresistance in the vicinity of their ferromagnetic transitions. This is because in the vicinity of the ferromagnetic transition, conduction electrons are scattered by magnetic fluctuations. Switching on a magnetic field supresses such fluctuations and this results in a reduction of such scattering and consequently, a reduction in the electrical resistivity.



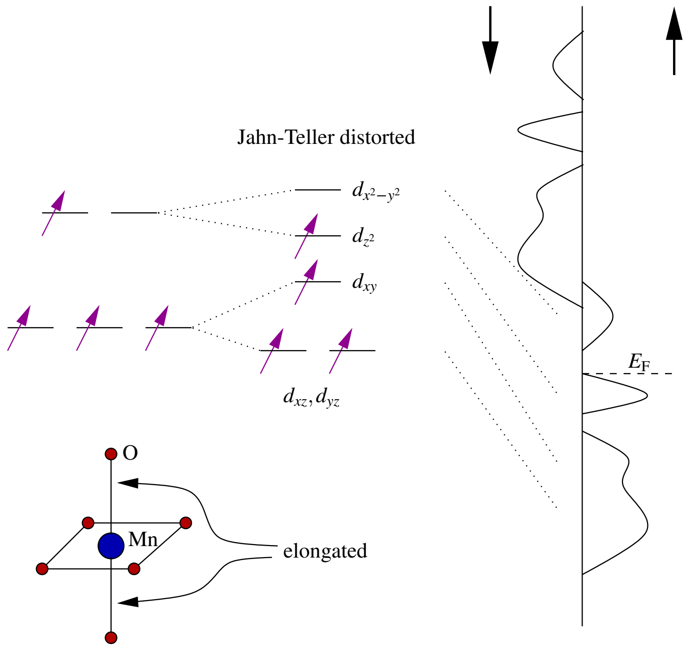
- In 1950, Jonker and van Santen in the Netherlands found that the perovskite $LaMnO_3$ which is an antiferromagnetic insulator, becomes metallic when La is substituted by Sr; in $La_{1-x}Sr_xMnO_3$, when x is around 0.3, the system becomes displays an insulator-metal transition on cooling. Concurrently, at the same temperature as the metal-insulator transition, the system becomes ferromagnetic:



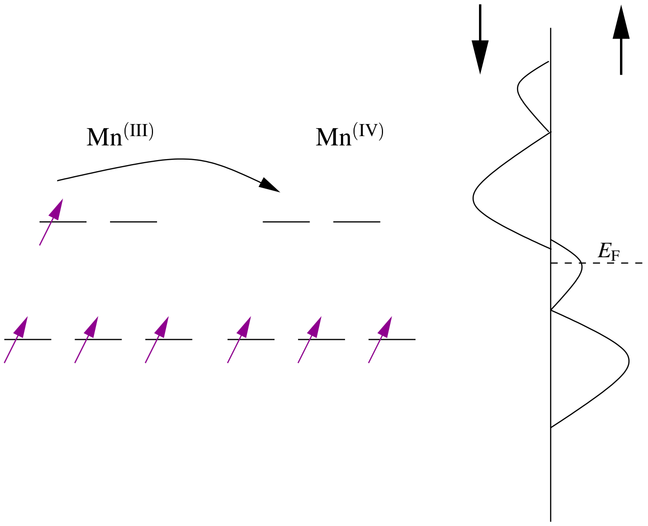
At T_C, the system becomes metallic [indicated by the change of temperature coefficient of resistance (TCR) from negative to positive] and ferromagnetic (indicated by a sharp rise in the magnetization).

The reson why this happens is called Zener Double Exchange (DEX).

- The electronic configuration of d^4 Mn in $LaMnO_3$ is octahedral and high spin with a Jahn-Teller distortion.

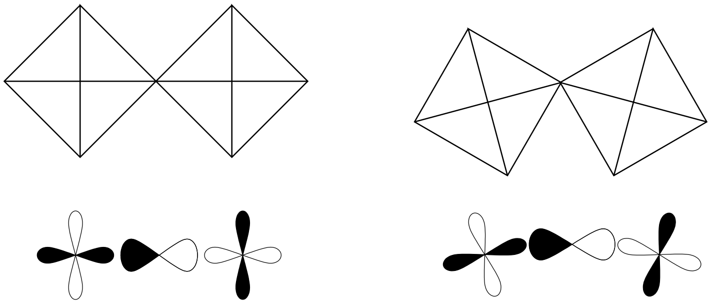


- The substitution of 30% Sr in the La site results in a change in the oxidation state according to $La^{3+}_{1-x}Sr^{2+}_{x}Mn^{(III)}_{1-x}Mn^{(IV)}_{x}O_3$ with $x = 0.3$. The removal of electrons from trivalent d^4 Mn results in a loss of most of the Jahn-Teller nature (the elongation of 2 Mn-O bonds in the MnO_6 octahedra) and the possibility that the e_g electron on one $Mn^{(III)}$ can hop to its neighboring $Mn^{(IV)}$.



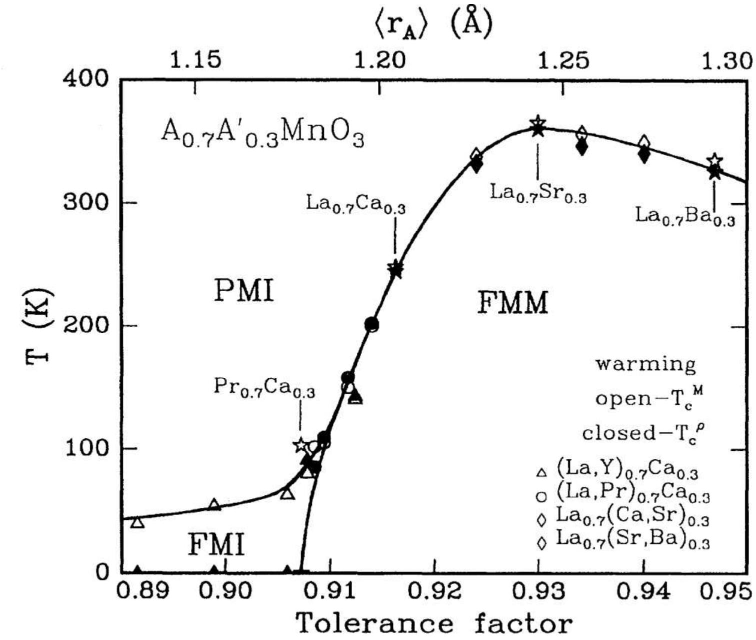
The important ingredient in the Zener DEX mechanism is that the electron retains a “memory” of its spin when it hops from one site to the next. Such hopping is therefore favored in the ferromagnetic state. This is why $La_{0.7}Sr_{0.3}MnO_3$ displays metallic behavior and ferromagnetism at the same time.

- What is the mechanism for the colossal magnetoresistance. Near the magnetic transition, when the spins are tending to line up, switching on a magnetic field helps align neighboring spins. Hopping from Mn$^{(\mathrm{III})}$ to neighboring Mn$^{(\mathrm{IV})}$ is therefore facilitated. In certain materials, the application of a 7 T magnetic field can result in a 13 order of magnitude decrease in the electrical resistivity (“turning wood into silver”)
- Issues in colossal magnetoresistance (CMR) manganese oxides:
  - The effect of oxidation state in $Ln_{1-x}A_xMnO_3$ where Ln is a trivalent rare-earth (Ln = La, Pr, Nd . . .) and A is an alkaline earth metal (A = Ca, Sr, Ba). The most studied compositions are $x \sim 0.3$, when about one-third of the Mn are in the 4+ oxidation state.
  - The effect of the perovskite tolerance factor. When the average size on the A site (the weighted average of $Ln_{1-x}A_x$) is small, t is small and the Mn-O-Mn bond angle deviates greatly from 180°. This results in the electrical resistivity being greater and the transition from insulator to metal taking place at lower temperatures.



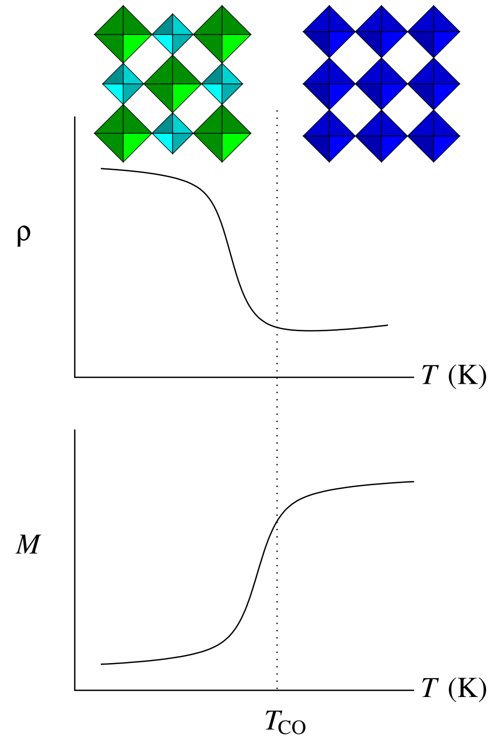
Mn-O-Mn near 180° Mn-O-Mn less than 180°

The reduction of the Mn-O-Mn bond angle because of tilting of octahedra (a consequence of small t) results in poorer overlap between orbitals (the figure shows $d_{x^2-y^2}$ on Mn and p_x on O). This makes the system a poorer metal.



From H. Y. Huang *et al.* *Phys. Rev. Lett* **75** (1995) 914. This plot shows the temperature at which the different compounds become ferromagnetic as a function of the average size of the A cation. The tolerance factor t, and the average 9-coordinate Shannon-Prewitt radii form the different ordinate (x) axes. Note how the highest transition temperature is found for a specific tolerance factor. PMI = paramagnetic insulator, FMM = ferromagnetic metal, FMI = ferromagnetic insulator.

- Charge ordering when $x = 0.5$: In compositions such as $\mathrm{La_{0.5}Ca_{0.5}MnO_3}$, when the amounts of $\mathrm{Mn^{III}}$ and $\mathrm{Mn^{IV}}$ are equal, there is the possibility of forming a crystalline ordering of two different kinds of octahedra. The material becomes an antiferromagnetic insulator at a certain temperature, called the *charge-ordering* temperature. Such a phase transition is also called Wigner crystallization or the Verweij transition.



Schematic diagram displaying the charge-ordering transition in a ferromagnetic metals such as $La_{0.5}Ca_{0.5}MnO_3$. Above the charge-ordring transition $T_{\rm CO}$, the MnO_6 octahedra are all equivalent, with an average Mn oxidation state of $Mn^{3.5+}$. Below $T_{\rm CO}$, the extra electron corresponding to $Mn^{\rm III}$ orders on alternate Mn (forming a rock-salt like arrangement) resulting in insulating behavior (upper plot) and antiferromagnetism (lower plot). The structure now has two kinds of ordered octahedra: large ones corresponding to $Mn^{\rm III}$ and small ones corresponding to $Mn^{\rm IV}$.